

"A method and apparatus for keeping constant the retention times in a gaschromatographic analysis"

TECHNICAL FIELD

- 5 The present invention relates to a method for maintaining the retention times of the components of a mixture to be analysed constant in an apparatus for gaschromatographic analysis provided with a capillary column, when there is a variation in the length of said capillary column and/or a variation in the output pressure from said column.

10 PRIOR ART

- For the analysis of a specimen of a given mixture in a gaschromatographic apparatus, a known practice is to use a capillary column, having predefined stationary phase and nominal dimensions, in which the mixture to be analysed is made to pass in the
15 gaseous state, by means of an inert carrier gas (carrier), at an appropriate temperature, or temperature profile in time, at which the column itself is kept.

- During passage of the gaseous mixture in the apparatus, the various components (or substances) have different times for traversing the
20 capillary column as their own constituent parts vary, and hence the various substances reach a detector, set downstream of the column, in different times. There is thus obtained a separation in time of the components of the mixture which enables evaluation of the presence of each individual substance present. The said traversing times are
25 referred to as retention times of the substances.

Consequently, downstream of the capillary column, there arrive, at different instants, different amounts of homogeneous substances, and the detector is able to measure the amounts of these substances, producing a graphic representation, referred to as chromatogram,

which shows a series of consecutive peaks. The peaks are plotted on a cartesian graph, on the ordinate of which is a scale of measurements proportional to the amount of the substance and on the abscissa of which is the time elapsing from introduction of the specimen into the apparatus.

Given a type of column and the operating conditions, the retention time is characteristic for each substance and constitutes the parameter used for identification of the individual substance (component) that is detected.

In everyday use of gaschromatographic apparatus, it is common practice to cut the capillary column for the purpose of excluding terminal portions thereof that could be degraded after numerous analyses. This degradation can derive from possible non-vaporized by-products present in the specimen that accumulate in the initial portion of the column and/or from the possible overheating of the terminal portion of the column inside the detector.

It is likewise common practice to change the type of detector downstream of the capillary column according to the particular requirements of the analysis. The different detectors that may be used can operate at different pressures, and in particular it is common practice to use detectors that operate at atmospheric pressure and detectors that operate in the presence of a vacuum (mass spectrometer).

The above modifications, which do not necessarily envisage any replacement of the column and which are particularly frequent during the use of the apparatus, lead to a variation in the conditions of analysis and cause a modification of the retention times for the different substances that make up one and the same mixture.

In other words, the analysis of one and the same mixture of substances

before and after the aforesaid modifications, i.e., before and after cutting of the capillary column and/or the variation in the output pressure from the column, involves, all the other conditions being equal, the variation in the retention times, this resulting in the detriment
5 of the identification of the components of the mixture under examination. The variation in the retention times thus imposes a recalibration of the apparatus and/or a modification of the parameters of analysis in order to render comparable the results obtained before and after said modifications, these being activities
10 which involve, in common practice, a considerable expenditure in terms of time and resources.

There is consequently a widespread requirement of having available a method and an apparatus which, by detecting small amounts indicating the state of the system, will be able to determine new
15 functional parameters that will lead, after variation in length of the column and/or in the output pressure, to obtaining chromatograms that are immediately comparable with one another, i.e., that will enable the retention times to be maintained constant for each component analysed.

20 For the above purpose, there is known a method, proposed in the U.S. patent No. US 6.036.747, which envisages, after detection of some state parameters prior to variation in the apparatus and setting of the new values of length of the column or output pressure, obtaining a value of the input pressure of the carrier gas to be imposed on the
25 system after said variations. This new value of the input pressure is calculated on the basis of three different formulae in relation to the initial value that the output pressure assumes. The method proposed is, however, somewhat complex to implement and, given the multiplicity of relations for calculation of the new value, does not always lead to

reliable values. The method moreover requires the knowledge of the geometrical parameters of the column (length and internal diameter), which are far from easy to measure with accuracy.

The patent EP-B-0.741.867, in the name of the present applicant,
5 teaches how to measure experimentally, by means of a test with just the carrier, a constant K that is a function of the geometrical parameters of the column used in the apparatus for gaschromatographic analysis, for the purpose of providing a simple and reliable method for controlling the flow rate in the
10 gaschromatographic apparatus itself. This patent right does not, however, contain any indications regarding the use of said constant K , defined also as the inverse of the pneumatic resistance of the column, in order to maintain the retention times constant as the geometrical parameters of the column vary or as the output pressure from the
15 latter varies, said pressure being determined by the detector used for the analysis.

A purpose of the present invention is to provide a method and an apparatus which, as the length of the column varies and/or the output pressure varies, enables the same retention times of the substances of
20 a mixture to be obtained before and after said variation, in the case where the temperatures of the column are maintained the same, instant by instant, starting from when the specimen is introduced into the apparatus.

Another purpose of the present invention is to provide a method and
25 an apparatus that will enable, starting from simple measurements of the state of the system, precise values of pressure and/or of flow rate of the carrier gas to be obtained, which are to be set after a variation in length of the column and/or in the output pressure of the carrier gas, for the purpose of obtaining the aforesaid same retention times

for the same substances, before and after said variations.

SUMMARY OF THE INVENTION

The above and further purposes are achieved by the method according to the first independent claim and the subsequent
5 dependent claims and by the apparatus according to the independent Claim 8 and the subsequent dependent claims.

According to the present invention, the method for obtaining the reproducibility of the retention times of the components of a mixture to be analysed in an apparatus for gaschromatographic analysis
10 provided with a capillary column when one of the following variations occurs: namely variation in the length of the column, or alternatively replacement of the column with a column having identical real specifications with the exception of the length, and/or variation in the pressure of the carrier gas at output from said column – envisages that
15 the temperature or temperature profile will be maintained unvaried, instant by instant, starting from the introduction of the mixture to be analysed into the apparatus, for each analysis of the mixture. The method moreover envisages that the pneumatic resistance of the column $KC_{old}=K(L_{old})$ is known prior to the aforesaid variations, the
20 analytical expression of which is

$$K(L_{old}) = \frac{256 \cdot L_{old}}{\pi \cdot d^4} \cdot \frac{\eta_0 \cdot P_{ref}}{T_{ref}^{1+\alpha}} \quad (9)$$

where:

d is the diameter of the column;

P_{ref} , T_{ref} are, respectively, the reference pressure and the
25 reference temperature (referred to the standard conditions);

η_0 is the viscosity of the carrier gas under the reference conditions;

L_{old} is the initial length of the column; and

α is the coefficient depending upon the type of carrier gas used;

and further envisages that, prior to the variations in the length of the column and/or in the output pressure, the pressure $p_{i,old}$ of the carrier gas will be detected at a point corresponding to the input section of the column, and the pressure $p_{o,old}$ of the carrier gas will be detected at a point corresponding to the output section of the column. Furthermore, after the aforesaid variations, the method envisages that the new pneumatic resistance of the column $KC_{new}=K(L_{new})$ will be detected, the analytical expression of which is

$$K(L_{new}) = \frac{256 \cdot L_{new}}{\pi \cdot d^4} \cdot \frac{\eta_0 \cdot P_{ref}}{T_{ref}^{1+\alpha}} \quad (5)$$

where:

L_{new} is the new length of the column;

and further envisages that the possible new pressure $p_{o,new}$ at output from the column will be selected.

Then the method according to the invention envisages calculation of a new input pressure $p_{i,new}$ or of a new mass flow F_{new} (referred to standard conditions) of the carrier gas, using the following relation:

$$\lambda = \frac{j_{old}}{j_{new}} \cdot g \cdot \frac{P_{o,new}}{P_{o,old}}$$

where:

$$g = \frac{K(L_{new})}{K(L_{old})} = \frac{L_{new}}{L_{old}}$$

$$j_{new} = \frac{3}{2} \cdot \frac{\left(\frac{P_{i,new}}{P_{o,new}} \right)^2 - 1}{\left(\frac{P_{i,new}}{P_{o,new}} \right)^3 - 1}$$

$$j_{old} = \frac{3}{2} \cdot \frac{\left(\frac{P_{i,old}}{P_{o,old}} \right)^2 - 1}{\left(\frac{P_{i,old}}{P_{o,old}} \right)^3 - 1}$$

and the setting of the new input pressure $p_{i,new}$ or of the new mass flow F_{new} of the carrier gas into said apparatus for gaschromatographic analysis in correlation to λ .

It may be noted that the pneumatic resistance KC (KC_{old} or KC_{new}) defined analytically above, and to which reference will be made in what follows, is for convenience of calculation the inverse of the constant \underline{K} defined in the above-mentioned patent EP-B-0.741.867, filed in the name of the present applicant.

BRIEF DESCRIPTION OF THE DRAWINGS

Described in what follows are some particular embodiments of the method according to the present invention and of an apparatus designed to implement one or more of said method, said embodiments being provided purely by way of non-limiting example, with the aid of the attached figures, in which:

Figure 1 is a block diagram of a particular embodiment of the method according to the present invention;

Figure 2 is a block diagram of another embodiment of the method according to the present invention;

Figure 3 is a diagram of an apparatus designed to implement the

method represented in Figure 1;

Figures 4a and 4b are, respectively, a chromatogram regarding the analysis of a given specimen with a capillary column 15 metres long and a chromatogram regarding the analysis, under the same temperature conditions, of the same specimen with the same capillary column shortened to approximately 13 metres; and

Figures 5a and 5b are, respectively, a chromatogram regarding the analysis of a given specimen with the use of a detector operating at atmospheric pressure (approximately 101 kPa) and a chromatogram regarding the analysis, under the same temperature conditions, of the same specimen with a detector operating in vacuum conditions (approximately 10^{-5} kPa).

DETAILED DESCRIPTION OF SOME EMBODIMENTS OF THE INVENTION

During gaschromatographic analysis of a given mixture in an apparatus provided with a capillary column, for any one component of said mixture, the retention time in a given column j can be defined as

$$t_{r,j} = t_{0,j} \cdot (1 + k_j)$$

where:

$t_{0,j}$ is the so-called "dead" time, defined by the following relation:

$$t_{0,j} = \frac{L_j}{\bar{u}_j}$$

k_j is a ratio of capacity (defined as "capacity factor");

L_j is the length of the column j ; and

\bar{u}_j is the mean linear velocity of the carrier gas in the column j .

Considering now two capillary columns, one designated by the

subscript "old" and the other by the subscript "new", which have the same internal diameter and the same stationary-phase thickness, it is possible to show that

$$\frac{t_{r,old}}{t_{r,new}} = \frac{t_{0,old}}{t_{0,new}}$$

- 5 whence it is found that the retention times of the same component in two columns which have only their lengths different are the same if the times t_0 in the two columns are the same.

However, the dead time t_0 in a given column of length L is defined, as already given above, as

10
$$t_0 = \frac{L}{\bar{u}}$$

where \bar{u} is the mean linear velocity of the carrier gas (carrier) in the column; and

L is the length of the column.

- Now, introducing the pneumatic resistance of a column, which can advantageously be calculated empirically, as emerges from the
 15 European patent EP-B-0.741.867, filed in the name of the present applicant, and which has the analytical expression

$$KC = \frac{256 \cdot L}{\pi \cdot d^4} \cdot \frac{\eta_{std} \cdot P_{std}}{T_{std}^{1+\alpha}} \quad (i)$$

where:

- 20 d is the diameter of the column;
 P_{std} and T_{std} are the reference pressure and the reference temperature, respectively (under standard conditions);
 η_{std} is the viscosity of the carrier gas under reference conditions;
 L is the length of the column;

α is the coefficient of dependence of the viscosity upon the temperature, which is a function of the particular type of carrier gas used (where $0 < \alpha < 1$);

it is found that, given the same diameter of the two columns ("old" and "new") which have only their lengths different, the following relation applies:

$$\frac{L_{new}}{L_{old}} = \frac{KC_{new}}{KC_{old}}$$

and consequently, by imposing $t_{0,1} = t_{0,2}$, we have

$$\frac{L_{old}}{u_{old}} = \frac{L_{new}}{u_{new}}$$

$$u_{new} = u_{old} \cdot \frac{KC_{new}}{KC_{old}} \quad (ii)$$

The above relation indicates that, in order to maintain the retention times of a given substance constant as the length of a column varies, but given the same diameter of the column and thickness of the stationary phase of the latter, it is sufficient to enter a new mean velocity of the carrier gas that is directly proportional – but for a constant that depends upon said variation in length – to the mean velocity of the carrier gas before the variation.

However, in a normal apparatus for gaschromatographic analysis it is not possible to set this mean velocity directly (unless the actual values of length and diameter of the column are accurately known), whilst it is common practice to enter the pressure p_i of the carrier gas at input to the column, or else the mass flow F of said gas.

Introducing now the corrective factor of the pressure gradient, defined as

$$j = \frac{3}{2} \cdot \frac{\left(\frac{p_i}{p_o}\right)^2 - 1}{\left(\frac{p_i}{p_o}\right)^3 - 1} \quad (\text{iii})$$

where p_i is the pressure of the carrier gas at input to the column; and
 p_o is the pressure of the carrier gas at output from the column,
the mean velocity of the carrier gas can be expressed as a function of
5 the velocity of output of the gas from the column u_o , as

$$\bar{u} = j \cdot u_o \quad (\text{iv})$$

But, the output velocity u_o can be expressed as a function of the flow
rate (measured under the effective thermodynamic conditions of the
apparatus) in the column as

$$10 \quad u_o = \frac{4}{\pi \cdot d^2} \cdot F_o^{T_{col}} \quad (\text{v})$$

where d is the diameter of the column; and

T_{col} is the temperature of the column,

and referring the flow rate to standard conditions (101 kPa, 20°C) via
the following relation:

$$15 \quad F = F_o^{T_{col}} \cdot \frac{T_{std}}{T_{col}} \cdot \frac{p_o}{p_{std}} \quad (\text{vi})$$

where T_{std} and p_{std} are, respectively, the standard temperature and
standard pressure; and

p_o is the output pressure from the column,

we have

$$20 \quad u_o = F \cdot \frac{T_{col}}{T_{std}} \cdot \frac{p_{std}}{p_{col}} \cdot \frac{4}{\pi \cdot d^2} \quad (\text{vii})$$

Consequently, introducing now the subscripts "old" and "new" to

designate, respectively, the column of initial length and the column of modified length, recalling that the real diameter is the same and assuming that the output pressure may vary, it is found (considering the ratio between velocity of the carrier gas at output from the column) that

$$\frac{u_{o,new}}{u_{o,old}} = \frac{F_{new}}{F_{old}} \cdot \frac{P_{o,old}}{P_{o,new}} \quad (\text{viii})$$

and considering now relation (ii), which imposes the constancy of the retention times, and the subsequent equation (iv), we have

$$\frac{u_{o,new}}{u_{o,old}} = \frac{F_{new}}{F_{old}} \cdot \frac{P_{o,old}}{P_{o,new}} = \frac{j_{old}}{j_{new}} \cdot \frac{KC_{new}}{KC_{old}} \quad (\text{ix})$$

where

$$j_{new} = \frac{3}{2} \cdot \frac{\left(\frac{P_{i,new}}{P_{o,new}}\right)^2 - 1}{\left(\frac{P_{i,new}}{P_{o,new}}\right)^3 - 1}$$

$$j_{old} = \frac{3}{2} \cdot \frac{\left(\frac{P_{i,old}}{P_{o,old}}\right)^2 - 1}{\left(\frac{P_{i,old}}{P_{o,old}}\right)^3 - 1}$$

i.e., designating as λ the following quantity:

$$\lambda = \frac{j_{old}}{j_{new}} \cdot g \cdot \frac{P_{o,new}}{P_{o,old}} \quad (\text{x})$$

where

$$g = \frac{KC_{new}}{KC_{old}} = \frac{L_{new}}{L_{old}} \quad (xi)$$

we obtain the following relation:

$$F_{new} = F_{old} \cdot \lambda \quad (xii).$$

This relation indicates that, to obtain the same retention times for one
 5 and the same substance, when the length of the capillary column is
 modified and/or the output pressure of the carrier gas is modified, it is
 necessary to enter a new mass flow F_{new} of the carrier gas
 proportional, via the parameter λ , to the mass flow F_{old} recorded, or
 calculated, prior to the aforesaid modifications.

10 It may be noted that relation (xii) is valid only in the case where the
 analyses performed before and after the variation in length of the
 column and/or the variation in output pressure are performed,
 maintaining the actual diameter of the column and the temperature
 (T_{col}) of the column constant instant by instant (starting from
 15 introduction of the mixture to be analysed).

Furthermore, as may be appreciated from the foregoing equations,
 the mass flow F depends strictly upon the temperature that the
 column assumes and consequently, in the case where for the analysis
 of a given specimen it were necessary to enter a program of
 20 temperatures in time, it would become necessary to calculate and
 control the new mass flow F_{new} , instant by instant.

Since frequently during an analysis the temperature follows a
 predefined temporal trend (and hence is a function of time), if the aim
 is to operate with a constant flow of the carrier gas, it will be necessary
 25 to detect, as the temperature varies, the quantity p_i and then
 calculate the quantity j . This requisite renders it more difficult to
 maintain the flow of the carrier gas under control, according to

relation (xii), in order to maintain the retention times constant.

It is, on the other hand, possible to express the flow rate F as a function of the pressures of the carrier gas at input to and output from the column, as follows:

$$F = \frac{p_i^2 - p_o^2}{KC \cdot T_{col}^{1+\alpha}} \quad (xiii)$$

and recalling that the program of the temperature T_{col} and the real diameter of the column are the same both before and after the variations in length of the column and/or in output pressure, we can write

$$\frac{p_{i,new}^2 - p_{o,new}^2}{p_{i,old}^2 - p_{o,old}^2} = \lambda \cdot g$$

i.e., we obtain

$$p_{i,new} = \sqrt{p_{o,new}^2 + \lambda \cdot g \cdot (p_{i,old}^2 - p_{o,old}^2)} \quad (xiv).$$

It may be noted that this relation does not depend upon the mass flow F and is consequently independent of the particular temperature profile followed in time for carrying out the analysis. That is, relation (xiv) does not presuppose calculation instant by instant of the input pressure of the carrier gas to be set in the apparatus after the variation in length of the column and/or in the output pressure.

Consequently, to obtain the same retention times of a substance as the length of the column varies and/or the output pressure of the carrier gas varies, under the hypothesis that the actual diameter of the column, the thickness of the stationary phase, and the temperature program are kept constant, it is sufficient to enter the new input pressure of the carrier gas, according to what is defined by relation (xiv).

Said relation (xiv), as likewise relation (xii), is not linear, i.e., since the quantity j_{new} depends upon $p_{i,\text{new}}$ and hence upon F_{new} , for the analytical solution of the two equations it is necessary to use a method of successive approximations. However, it may readily be shown that
 5 this method converges in a few passages towards an optimal solution.
 From the relations given above, it is evident for a person skilled in the branch that, given the inaccuracy (and sometimes the impossibility on account of the small dimensions of the capillary columns) of a direct measurement of the real geometrical characteristics of the column
 10 (length and diameter) before and/or after the variations in length of the column and/or in output pressure, it is extremely advantageous to be able to detect the pneumatic resistance of the column KC , which, since it may be derived empirically (see the patent EP-B-0.741.867) by means of a blank test of the apparatus, i.e., with just the carrier,
 15 enables precise calculation of the ratio g (equation (xi)) and of the parameter λ (equation (x)).

In particular, the value of KC of equation (i) can be determined, as may be deduced from relation (xiii) by measuring, during a blank test, the input flow F_{st} referred to the standard conditions, the temperature
 20 T_{col} of the column, and the input and output pressures, p_i and p_o respectively, of the column, according to the following relation:

$$KC = \frac{p_i^2 - p_o^2}{F_{st} \cdot T_{col}^{1+\alpha}} \quad (\text{xiii.bis}).$$

From what has been discussed above, it is found that in the case where, in laboratory practice, it becomes necessary to cut the column
 25 or vary the type of detector set downstream of the column itself, and hence vary the output pressure, it is sufficient to measure - prior to the variation - the quantities:

- KC_{old} , which is the pneumatic resistance of the column (possibly measured by means of a blank test), and the analytical expression of which is, analogously to equation (i), as given below:

$$5 \quad KC_{old} = K(L_{old}) = \frac{256 \cdot L_{old}}{\pi \cdot d^4} \cdot \frac{\eta_0 \cdot P_{ref}}{T_{ref}^{1+\alpha}} \quad (i.bis)$$

wherein:

- L_{old} is the length of the column before a variation thereof;
- $p_{i,old}$, which is the input pressure of the carrier gas (measurable);
- 10 - $p_{o,old}$, which is the output pressure of the carrier gas (known);
- possibly (if we proceed using equation (xii)) F_{old} or T_{col} , which are the mass flow in standard conditions and the effective temperature of the column, respectively;

15 and, following upon the variations, the quantities:

- $p_{o,new}$, which is the expected output pressure (known); and
- KC_{new} , which is the new pneumatic resistance of the column (measured for example according to what is described in EP-B-0.741.867) and the analytical expression of which is:

$$20 \quad KC_{new} = K(L_{new}) = \frac{256 \cdot L_{new}}{\pi \cdot d^4} \cdot \frac{\eta_0 \cdot P_{ref}}{T_{ref}^{1+\alpha}} \quad (i.ter);$$

where L_{new} is the length of the column after its (possible) variation,

25 in order to obtain from relations (xiv) or (xii) the new values $p_{i,new}$ (input pressure) or F_{new} (flow rate under standard conditions) with

which to set the apparatus to obtain the constancy of the retention times.

With reference to Figure 1, described herein is a method for maintaining the retention times constant for the analysis of a mixture after the variation in length of the capillary column and/or the variation in the output pressure of the carrier gas, where the length of the column is not known, but its initial pneumatic resistance KC_{old} (for example, measured via an experimental blank test) is known, and in which there is available an apparatus, such as the one represented schematically in Figure 3, which enables maintaining the input pressure p_i of the carrier gas constant.

The method envisages (step 101) recording, prior to the aforesaid variation or variations, the pressure of the carrier gas at input $p_{i,old}$ and the pressure of the gas at output $p_{o,old}$, the latter depending upon the type of device for analysis that is set downstream of the capillary column.

After the variations in the length of the column and/or in the output pressure (step 102), it is necessary to determine again (step 103) the constant of resistance of the column KC_{new} . Said value KC_{new} can be determined automatically by the apparatus for analysis, by means of, for example, a so-called blank test, i.e., by causing only carrier gas to flow, in stabilized conditions of flow rate, and subsequently measuring or setting the values T_{col} , p_i , F (and possibly p_o if this is not known), according to relation (xiii).

Once the value of KC_{new} is thus known, which depends, under the hypotheses made, uniquely upon the new length assumed by the column (see relation (i)), it is possible to set conveniently (step 104), using equation (x), the analytical expression given by relation (xiv) and then solve the latter by means of successive approximations.

The value of $p_{i,new}$ thus calculated must now be set (step 105) into the apparatus for analysis as new input pressure of the carrier gas in order to maintain the retention times of the various components of the mixture to be analysed constant before and after the aforesaid variations in length of the column and/or in output pressure of the carrier gas.

In the event of the variation undergone by the apparatus consisting only of the variation in output pressure, it would not be necessary to re-determine the constant KC of the column (which remains unvaried), and thus step 103 should not be executed.

As already mentioned, the method described can be implemented using the apparatus for gaschromatographic analysis represented schematically in Figure 3, in which there are present, on the line for introduction of the carrier gas, a device 1 for detection of the input pressure of the carrier, and means 2 for regulating said pressure, as well as an injection system 3 for input of the mixture to be analysed, which at output directs the flow of gas towards a capillary column 6.

The apparatus moreover comprises an oven 4, the temperature of which is regulated by a control device 5, and a capillary column 6 of length L or pneumatic resistance KC known, housed within the oven 4 itself. Downstream of the column 6, there is moreover present a detector 7 for the gases at output from the column, which is designed to measure the amount of the gases that flow from the column 6 itself.

The apparatus moreover comprises storage and processing means 8 (usually an electronic processor), which interface both with the operator and with the device for detection of the pressure 1, and govern the control device 5 and the means 2 for regulation of the

input pressure of the carrier. During normal operation, the constant of resistance KC_{old} of the column 6, is stored in these means 8, and the input pressure of the carrier gas $p_{i,new}$ is measured and stored.

5 Consequently, as the length of the column 6 and/or the output pressure of the carrier gas vary/varies following upon the replacement of the detector 7, the operator sets, and starts execution of, an appropriate control program, possibly already present in the electronic processor 8, which has the job of determining, for example via a blank test as described in EP-B-
10 0.741.867, the new value of the constant KC_{new} and of prompting the operator for the possible new value of the output pressure $p_{o,new}$.

Then, the electronic processor 8 calculates, via successive approximations, the new value $p_{i,new}$ that the input pressure of the
15 carrier must assume so that the retention times will remain constant for each substance, and, when a new analysis is performed, sets said new pressure $p_{i,new}$ by acting on the means 2 for regulating the pressure of the carrier at input.

Alternatively, or in addition, the apparatus may comprise means for
20 measuring the mass flow F of the carrier gas, possibly referred to standard conditions, and means for regulating this flow (not illustrated). There may likewise be provided a detector for detection of the output pressure of the carrier gas (not illustrated).

Figure 2 illustrates, instead, a method for maintaining the retention
25 times constant after variation in the length of the column and/or in the output pressure of the carrier, whereby it is envisaged to control the mass flow of the carrier and whereby the value KC_{old} of the constant of resistance of the column is known.

In a way similar to the method illustrated in Figure 1, there is

5 envisaged, a step 201 in which, prior to the variations of the apparatus, there is carried out the measurement of the input pressure $p_{i,old}$ of the carrier, of the output pressure $p_{o,old}$ (if it is not known already) and, unlike the method illustrated in Figure 1, of the mass flow F_{old} , referred to standard conditions. The latter detection, as may readily be understood from the analysis of relation (xiii), can alternatively be replaced by measuring the temperature T_{col} of the column in order to calculate the quantity F_{old} itself. If the operation is carried out at constant flow, as the temperature T_{col} varies also the input pressure p_i will vary, which hence is to be calculated instant by instant.

10 After variation in length of the column and/or in the output pressure of the carrier (step 202), the subsequent step 203 envisages redetermining the constant KC_{new} only if the variation in length of the column has occurred, and step 204 envisages calculating the new mass flow F_{new} (equation (xii)) under standard conditions, whereby constancy of the retention times is to be obtained.

Finally, step 205 envisages this value F_{new} being set into the apparatus for subsequent analyses.

20 The method represented schematically in Figure 2, on account of its dependence upon the temperature variation during time, which renders it substantially suitable only for analysis at constant temperature, is rarely used.

25 Consequently, provided in what follows are two examples in which the retention times for a mixture to be analysed are kept constant, as the length of the column varies and the output pressure varies respectively, operating with constant input pressure of the carrier.

EXAMPLE 1

A mixture underwent analysis to identify the amounts of

compounds from C10 to C30 (i.e., mixtures of linear hydrocarbons with a number of carbon atoms ranging from 10 to 30) in a gaschromatographic apparatus provided originally with a capillary column of the 15m x 0.25mm x 0.25 μ m DB5 type. The carrier gas was helium (He) maintained at a constant input pressure (relative pressure: 80 kPa), the temperature of the column followed a program that passed from 70°C to 300°C at a rate of 10°C/min, and the pneumatic resistance of the column was $KC_{old} = 0.6484$. The output pressure was equal to the atmospheric pressure (101 kPa), and the results of the analysis are represented in the chromatogram provided in Figure 4a (the ordinate represents an amount correlated to the amount of gas as it passes the detector downstream of the column, and the abscissa the time elapsed). Each of the peaks, which follow one another at determined time intervals, represents the measured amount of a certain component (see Table 1).

The column was then cut, by a length of approximately 2 metres, and the measurement of the pneumatic resistance was repeated, via a blank test (i.e., only with the carrier) according, for example, to the teachings of EP-B-0.741.867, and the result was $KC_{new} = 0.5649$. The output pressure was not modified.

Calculation of the new input pressure (according to equation (xii)) led to defining the value $p_{i,new} = 60$ kPa (relative pressure) as a new value of the input pressure of the carrier.

The same mixture was then analysed after variation of the length of the column, setting the new value of $p_{i,new}$ and maintaining the temperature program constant. The results of the analysis are given in the chromatogram in Figure 4b.

A numeric representation of the retention times in the two cases is

provided in Table 1.

Component	Retention times (original column) (min)	Retention times (cut column) (min)	Difference (absolute value) (min)
C10	2.00	1.98	0.02
C12	4.38	4.35	0.03
C14	7.05	7.03	0.02
C16	9.57	9.55	0.02
C18	11.87	11.85	0.02
C20	13.96	13.94	0.02
C24	17.63	17.61	0.02
C30	22.19	22.19	0.00

Table 1

5 EXAMPLE 2

A mixture underwent analysis to identify the amount of compounds from C10 to C30 (i.e., of linear hydrocarbons with a number of carbon atoms ranging between 10 and 30) in a gaschromatographic apparatus having a capillary column of the 30m x 0.32mm x 0.25 μ m DB5 type, using a flame-ionisation detector (FID), operating at atmospheric pressure (101 kPa). The carrier gas was helium (He) maintained at a constant input pressure (relative pressure: 135 kPa), the temperature of the column followed a program that passed from 80°C to 320°C at a rate of 20°C/min, and the constant of resistance of the column was $KC_{old} = 0.6459$. The results of the analysis are represented in the chromatogram provided in Figure 5a, and the numeric evaluation of the retention times is given in Table 2.

The FID was then replaced by a mass spectrometer (MS), operating under vacuum conditions ($p_{o,new} = 10^{-5}$ kPa), and the column remained unaltered (i.e., the pneumatic resistance of the column was not modified $KC_{old} = KC_{new}$).

5 Calculation of the new input pressure (according to equation (xii)), on the basis of the new output pressure $p_{o,new}$, led to the new value $p_{i,new} = 70$ kPa (relative pressure) of the input pressure of the carrier. Note that not necessarily, when a mass spectrometer (operating under vacuum conditions, at approximately 10^{-5} kPa) is used, must
10 the output pressure be known with precision, in so far as for values smaller than 1 kPa its absolute value no longer substantially affects the result of the calculation. For the purposes of calculation, the output pressure, when it approaches vacuum conditions, may consequently be assumed as being equal to 10^{-5} kPa, whatever its
15 real value may be.

The same mixture was then analysed after the detector was replaced, setting the new value of $p_{i,new}$ and maintaining the temperature program constant. The results of the analysis are given in the chromatogram in Figure 5b.

20 A numeric representation of the retention times in the two cases is provided in Table 2.

Component	Retention times (atmospheric- pressure detector (FID)) (min)	Retention times (detector under vacuum conditions (MS)) (min)	Difference (absolute value) (min)
C10	2.10	2.12	0.02
C12	3.54	3.57	0.03

C14	4.99	5.02	0.03
C16	6.30	6.33	0.03
C18	7.49	7.51	0.02
C20	8.57	8.58	0.01
C24	10.46	10.47	0.01
C30	12.81	12.81	0.00

Table 2